

# The effect of water vapor on the performance of commercial polyphenylene oxide and Cardo-type polyimide hollow fiber membranes in CO<sub>2</sub>/CH<sub>4</sub> separation applications

M. Pourafshari Chenar<sup>a</sup>, M. Soltanieh<sup>a,\*</sup>, T. Matsuura<sup>b</sup>, A. Tabe-Mohammadi<sup>b,1</sup>, K.C. Khulbe<sup>b</sup>

<sup>a</sup> Department of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran, Iran

<sup>b</sup> Industrial Membrane Research Institute, Department of Chemical Engineering, University of Ottawa, Ottawa, Ont., Canada K1N 6N5

Received 24 May 2006; received in revised form 14 August 2006; accepted 27 August 2006

Available online 1 September 2006

## Abstract

The effects of water vapor on CO<sub>2</sub>/CH<sub>4</sub> separation using commercially available poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and Cardo-type polyimide hollow fiber membranes were investigated. Pure methane and CO<sub>2</sub>/CH<sub>4</sub> mixture permeation experiments were carried out in the absence and presence of water vapor (60% RH). Pure methane permeance decreased in the presence of water vapor for both membrane types. The decrease was 28% for hydrophilic Cardo-type polyimide and 6% for hydrophobic PPO membranes.

The decline in the permeance was also observed for CO<sub>2</sub>/CH<sub>4</sub> mixture separation through both membranes. However, selectivities of the two membranes were affected differently by water vapor. The Cardo-type polyimide membrane exhibited 43% decline in the permeances of both CO<sub>2</sub> and CH<sub>4</sub>, which resulted in an unchanged selectivity in the presence and absence of water vapor. The PPO membrane, on the other hand, showed different rates of decline for the two gases. While CO<sub>2</sub> permeance decreased by 11%, CH<sub>4</sub> experienced an average of only 4% decrease in permeance. Therefore, the selectivity of PPO membrane significantly declined in the presence of water vapor. It was also observed that the permeance of pure CH<sub>4</sub> was partially recovered when the experiment was conducted after a series of experiments with wet gas mixtures.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Commercial membranes; Gas separation; Methane; Carbon dioxide; Water vapor; Hollow fiber; Natural gas

## 1. Introduction

Natural gas is a vital component of the world's supply of energy. It is one of the cleanest, safest, and most useful types of energy sources. In the recent years, due to the sharp increase in the price of oil, natural gas and processes related to its purification have attracted more attention. Membrane-based treatment is one of the most promising processes in this industry. Tabe-Mohammadi [1] presented a brief history of membrane natural gas separation technologies and discussed the theoretical aspects of the process.

Hybrid systems, consisting of a membrane process for bulk separation followed by a secondary process such as gas absorp-

tion for final purification, have been proven to be technically and economically superior to the stand-alone systems [2,3]. Because the size and the cost of an industrial membrane process is directly governed by its permeation rate and selectivity, a considerable portion of research efforts is devoted to improving these two characteristics of membranes. Pourafshari Chenar et al. [4] studied the CO<sub>2</sub>/CH<sub>4</sub> separation properties of two of the most promising membranes, namely, Cardo-type polyimide and PPO membranes for CO<sub>2</sub>/CH<sub>4</sub> separation applications. The latter study, based on single gas permeation and gas mixture separation experiments concluded that both Cardo-type polyimide and PPO hollow fiber membranes are suitable for CO<sub>2</sub>/CH<sub>4</sub> separation. It was also exhibited that industrially favorable natural gas treatment properties could be obtained using a hybrid system that combines a membrane cascade and an absorption unit. The membrane cascade includes both Cardo-type polyimide and PPO membranes and is responsible for the bulk removal of CO<sub>2</sub>. The absorption unit further refines the gas stream and brings it to the pipeline grade.

\* Corresponding author. Tel.: +98 21 6616 5417; fax: +98 21 6602 2853.

E-mail addresses: [msoltanieh@sharif.edu](mailto:msoltanieh@sharif.edu), [msoltanieh@sina.sharif.ac.ir](mailto:msoltanieh@sina.sharif.ac.ir) (M. Soltanieh).

<sup>1</sup> Present address: Ministry of the Environment, Environmental Sciences and Standards Division, 40 St. Clair Avenue, West Toronto, Ont., Canada M4V 1M2.

Poly (2,6-dimethyl-1,4-phenylene oxide)      Cardo-type Polyimide

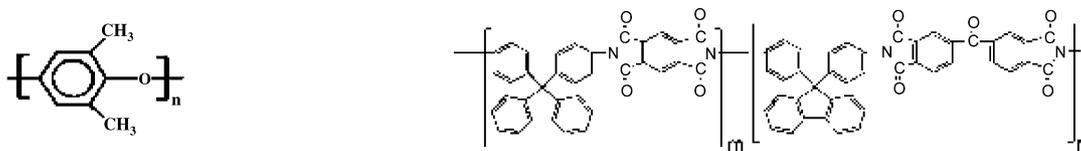


Fig. 1. Chemical structure of polyphenylene oxide and Cardo-type polyimide membranes [5,6].

Among the glassy polymers, Cardo-type polyimide and PPO possess excellent separation properties that make them suitable candidates for gas separation. The polyimide hollow fiber membranes that were developed for CO<sub>2</sub>/N<sub>2</sub> separation by “Research Institute of Innovative Technology for the Earth” (RITE, Japan) were proved to be good candidates for CO<sub>2</sub>/CH<sub>4</sub> separation as well due to their high selectivities in comparison with other glassy membranes [4]. Kazama et al. [5] have reported CO<sub>2</sub>/N<sub>2</sub> selectivity by using the same type of membrane. Story and Koros [6] have measured the CO<sub>2</sub>/CH<sub>4</sub> selectivity for cellulose acetate and polysulfone membranes. Kazama et al. [5], Tokuda et al. [7] and Karashima et al. [8] compared Cardo-type polymers with commercial polymers in respect to CO<sub>2</sub>/N<sub>2</sub> separation and CO<sub>2</sub> permeability and they showed the outstanding properties of these polymers with respect to other commercial membranes. A comparison between the CO<sub>2</sub>/CH<sub>4</sub> selectivity measured in this work and those reported in the literature will be made in the results and discussion.

On the other hand, PPO is a suitable candidate for a wide range of industrial gas separation applications. PPO is a linear amorphous thermoplastic with glass transition temperature ( $T_g$ ) ranging from 212 to 218 °C. Due to the presence of the phenyl rings, PPO is hydrophobic in nature and has excellent resistance to water, acids, alcohols, steam and bases [9]. It has been reported that, amongst all glassy polymers, PPO shows one of the highest permeabilities to gases [6,9–13]. The high permeability has been attributed to the absence of polar groups in the main chain of PPO [13].

An important factor governing the separation properties of any industrial application of membrane is the presence of other contaminants in the stream. The current study was focused on the effects of water vapor on the performance of Cardo-type polyimide and PPO membranes in CO<sub>2</sub>/CH<sub>4</sub> separation experiments.

Water vapor is frequently present in mixed gas streams and affects membrane performance significantly. As noted by Koros et al. [14], a very low partial pressure of a condensable species, such as water, in the feed stream can significantly reduce the permeability of a given constituent relative to its permeability as a pure component. It was also shown that in a gas mixture, competition by various penetrants to occupy the unrelaxed volume fraction of the polymer is a major factor in determining the permeability of a membrane. Such an effect may cause significant depression in sorption of both gases in binary mixtures.

Other investigations on the effects of water vapor on membrane performance indicated that in almost all cases water vapor retarded permeabilities of other components [8,15–19]. Pye et al. [15] investigated the effect of water vapor in the feed stream

and noted that a partial pressure of only 15 mm Hg of water vapor in a feed stream consisting of a 50/50 molar mixture of H<sub>2</sub> and CH<sub>4</sub> at 1 atm upstream pressure significantly depressed the permeabilities of both H<sub>2</sub> and CH<sub>4</sub>. It was stated that the presence of this small amount of water vapor in the mixed gas can reduce both fast gas (H<sub>2</sub>) and slow gas (CH<sub>4</sub>) permeabilities by as much as 20–60%.

Kruczek and Matsuura [17] stated that even the room humidity may affect the membrane performance. They studied the effects of relative humidity (RH) and hydrophilicity of polymer on gas separation and found that O<sub>2</sub> permeance was greater in winter (low RH) than in summer (high RH). It was also mentioned that CO<sub>2</sub> permeance, in contrast to other component, increased in the summer (high RH). Furthermore, it was shown that when the membrane is hydrophobic, e.g., PPO, water vapor pressure did not affect the membrane separation performance and no difference was observed in gas transport properties obtained from constant pressure system and constant volume separation systems.

Chern et al. [18] investigated CO<sub>2</sub> permeability through Kapton polyimide at 60 °C in the presence and absence of water vapor in the feed and found that CO<sub>2</sub> flux was depressed by the presence of water vapor.

Funk et al. [19] stated that moisture levels higher than 20% could cause irreversible cellulose acetate membrane compaction.

In the light of the above discussion and the fact that the raw natural gas is saturated in water, it was the objective of the present study to investigate the influence of water vapor on the permeability and selectivity of two available hollow fiber membranes, namely Cardo-type polyimide membrane and PPO for CO<sub>2</sub>/CH<sub>4</sub> applications. Furthermore, the extent to which the hydrophilicity and hydrophobicity of the two membranes affect the performance of these membranes was also studied.

## 2. Experimental

### 2.1. Materials and modules

The Cardo-type polyimide hollow fiber module was generously supplied by RITE, Japan. The inside and outside diameters of fibers were 370 and 500 μm, respectively.

The commercially available PPO hollow fibers were generously supplied by Aquilo Gas Separation B.V., The Netherlands (Parker Filtration and Separation B.V., The Netherlands). The inside and outside diameters of hollow fibers were 370 and 520 μm, respectively. The chemical structures of the two mem-

Table 1  
Cardo-type polyimide and PPO modules and hollow fibers specifications

| Module name | Membrane type | Hollow fiber parameters           |                                    | Module specifications |                                   |
|-------------|---------------|-----------------------------------|------------------------------------|-----------------------|-----------------------------------|
|             |               | Inside diameter ( $\mu\text{m}$ ) | Outside diameter ( $\mu\text{m}$ ) | No. of fibers         | Permeation area ( $\text{cm}^2$ ) |
| RITE-A      | Cardo-type PI | 370                               | 500                                | 135                   | 416                               |
| PPO#1       | PPO           | 370                               | 520                                | 10                    | 49                                |

brane types and the specifications of the two membrane modules are shown in Fig. 1 and Table 1, respectively.

The PPO module was assembled by loading a bundle of 10 fibers in a shell and tube structure. Although the dense selective layer of PPO hollow fibers was on the outside, in this study, the feed gas was introduced inside the fibers and permeate was collected outside. The permeances, however, were calculated based on the outer surface area of the hollow fibers.

Ultrahigh purity  $\text{CO}_2$  and  $\text{CH}_4$  and  $\text{CO}_2/\text{CH}_4$  gas mixtures (5%, 10% and 24.6%  $\text{CO}_2$ –balance  $\text{CH}_4$ ) were purchased from Praxair Distribution Inc., Canada.

## 2.2. Gas permeation experiments

The performance of hollow fiber modules in the presence and absence of water vapor were tested using a membrane gas separation system illustrated schematically in Fig. 2. The experiments were conducted at 7.9 bar absolute feed pressure (100 psig) and 30 °C. The sequence of experiments is given in Table 2.

The permeate, rich in  $\text{CO}_2$  (and water), was collected at atmospheric pressure, while a  $\text{CH}_4$ -rich retentate was collected at a pressure approximately equal to that of the feed.

For the dry gas experiments, either pure methane or  $\text{CO}_2/\text{CH}_4$  gas mixture was supplied from a cylinder to the bore side of the hollow fibers. In the case of wet gas experiments the feed gas at the operating pressure and temperature was saturated with water vapor by bubbling it through water in a saturator before feeding it to the hollow fibers.

The entire system except the saturator was placed in a temperature-controlled chamber with air circulation. The temperature of the saturator was maintained at 25 °C (5 °C below the temperature of the gas separation system), in order to prevent condensation of water in the system.

The permeation rate was measured by a bubble-flow-meter and the retentate flow rate was measured by a wet-test-meter.

Table 2  
Sequence of permeation experiments with dry and wet gas streams

|   | Feed $\text{CO}_2$ and $\text{CH}_4$ concentrations |                       | Feed $\text{H}_2\text{O}$ concentration |
|---|-----------------------------------------------------|-----------------------|-----------------------------------------|
|   | $\text{CH}_4$ (vol.%)                               | $\text{CO}_2$ (vol.%) | $\text{H}_2\text{O}$ (vol.%)            |
| 1 | 100                                                 | 0                     | 0                                       |
| 2 | 95                                                  | 5                     | 0                                       |
| 3 | 90                                                  | 10                    | 0                                       |
| 4 | 75.4                                                | 24.6                  | 0                                       |
| 5 | 99.7                                                | 0                     | 0.27                                    |
| 6 | 94.7                                                | 5.0                   | 0.30                                    |
| 7 | 89.7                                                | 10.0                  | 0.33                                    |
| 8 | 75.2                                                | 24.5                  | 0.31                                    |

The stage-cut was controlled by a metering valve installed at the retentate side.

The compositions of the retentate and permeate streams were determined by a gas chromatograph (Varian 3400) equipped with a thermal conductivity detector (TCD) and a “HayeSep Q” column. The compositions were corrected using thermal response factors, TRFs. The TRF values were carefully calculated for each gas following Dietz’s method [20].

## 3. Theory

The permeance of gas  $i$ ,  $(P/\ell)_i$ , is defined as the pressure-normalized flux of a gas through a membrane:

$$\left(\frac{P}{\ell}\right)_i = \frac{Q_P y_i}{(p_F \bar{x}_i - p_P y_i)A} \times 10^6 \quad (1)$$

Selectivity of gas  $i$  over gas  $j$ ,  $\alpha_{ij}^\circ$ , is defined as the ratio of permeance of gas  $i$  over gas  $j$ :

$$\alpha_{ij}^\circ = \frac{(P/\ell)_i}{(P/\ell)_j} \quad (2)$$

Separation factor of gas  $i$  over gas  $j$ ,  $\alpha_{ij}$ , is defined as the ratio of the concentration of gas  $i$  in the permeate to that in the feed relative to the same ratio for gas  $j$ :

$$\alpha_{ij} = \frac{y_i/\bar{x}_i}{y_j/\bar{x}_j} \quad (3)$$

where  $(P/\ell)_i$  is the permeance of gas  $i$ , GPU (1 GPU =  $10^{-6} \text{ cm}^3$  (STP)/ $\text{cm}^2 \text{ s cm Hg}$  =  $3.35 \times 10^{-10} \text{ mol/m}^2 \text{ s Pa}$ ),  $y_i$  the component mole fraction of gas  $i$  at permeate outlet,  $p$  the pressure (cm Hg),  $Q_P$  the permeation rate,  $\text{cm}^3$  (STP)/s,  $A$  the permeation area of the membrane ( $\text{cm}^2$ ), and  $\bar{x}_i$  and  $\bar{x}_j$  are the logarithmic average mole fractions of gases  $i$  and  $j$  in the feed-side and are calculated as

$$(\bar{x}_i)_{\ln} = \frac{x_{i,F} - x_{i,R}}{\ln(x_{i,F}/x_{i,R})} \quad (4)$$

where  $x_i$  is the component local mole fraction of gas  $i$  in the feed-side. Subscripts F and R denote feed and retentate, respectively.

For gas mixtures, the stage-cut ( $\theta$ ) was calculated as follows

$$\theta = \frac{Q_P}{Q_P + Q_R} \quad (5)$$

where  $Q_R$  is the retentate flow rate ( $\text{cm}^3$  (STP)/s).

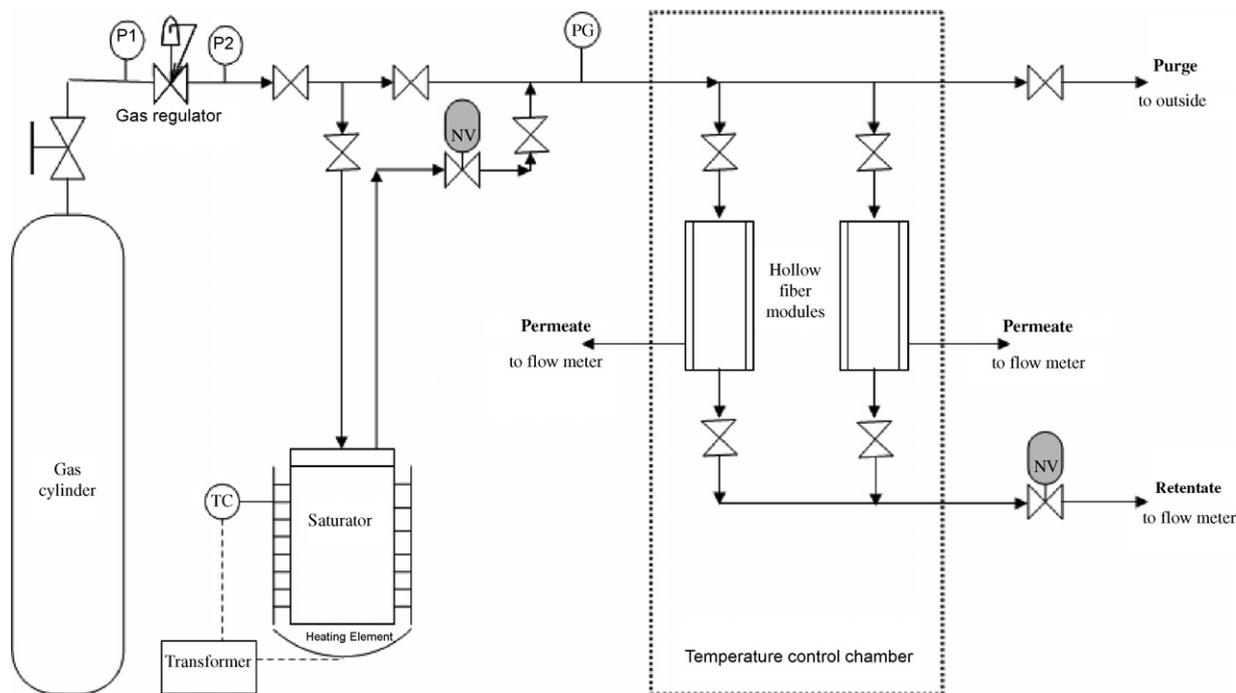


Fig. 2. Schematic diagram of the constant pressure membrane testing system.

## 4. Results and discussion

### 4.1. Cardo-type polyimide hollow fiber membranes

In this study, a partial pressure of around 0.024 bar (0.3 psi or 18 mm Hg) of water vapor was introduced into a stream of pure CH<sub>4</sub> or CO<sub>2</sub>/CH<sub>4</sub> mixtures at a total pressure of approximately 7.9 bar (100 psig). The permeability and selectivity results were then compared with those obtained from dry CH<sub>4</sub> and CO<sub>2</sub>/CH<sub>4</sub> mixtures. The reported data are the average of the last three readings that were obtained after steady state was reached. For this module, the steady state was reached after 5 h.

The stage-cut was set at 5% for all the gas mixtures experiments, except for high CO<sub>2</sub> concentration mixture (24.6% CO<sub>2</sub>), in which it was set at 15%.

Fig. 3 shows the CO<sub>2</sub> and CH<sub>4</sub> permeances as functions of CO<sub>2</sub> volume percent in the feed for both dry and wet experiments. As shown, the curves of permeances for dry and wet series of experiments are parallel and the permeances for both CO<sub>2</sub> and CH<sub>4</sub> increased with CO<sub>2</sub> volume percent. The latter can be attributed to the plasticization effect of this gas, which has previously been discussed elsewhere [4]. The similarity in the shapes of the curves in Fig. 3 implied that the presence of water did not affect plasticization of the membrane. On the other hand, the permeances of both CO<sub>2</sub> and CH<sub>4</sub> gases declined by 43% when hollow fibers were exposed to water vapor. Similar results were obtained with pure CH<sub>4</sub> in the absence and presence of water vapor. Pure methane permeance was decreased by 28% from 1.76 to 1.26 GPU.

Fig. 4 shows the effect of water vapor on the separation efficiency (separation factor and selectivity) of Cardo-type polyimide hollow fiber module. Because the permeances of both CO<sub>2</sub> and CH<sub>4</sub> declined at the same rate the CO<sub>2</sub>/CH<sub>4</sub> selectivity and

separation factor, as shown in Fig. 4, remained almost constant after the membrane was exposed to water vapor.

The competition of mixed penetrants for sorption sites and transport pathways associated with unrelaxed volume in glassy polymers is a general feature of gas/glassy polymer systems especially for high affinity components. Therefore, in the presence of high affinity water the permeability of membrane to CO<sub>2</sub> and CH<sub>4</sub> decreases due to the sorption of water vapor in the polymer, which effectively reduces the microvoid availability of the dense selective layer of membrane, hence available diffusion paths for other gases.

Sorption of water may result in swelling of the polymer matrix. It was stated that the presence of water vapor in some instances may accelerate the permeation rate of some gases [9,17], while in most cases the reverse effect is observed.

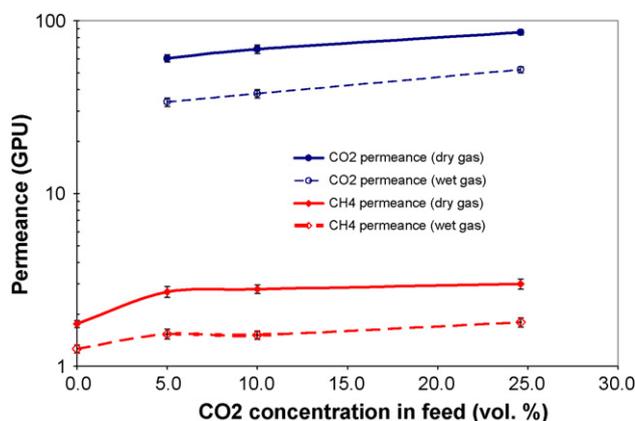


Fig. 3. CO<sub>2</sub> and CH<sub>4</sub> permeances vs. feed CO<sub>2</sub> concentration in the presence and absence of water vapor. Cardo-type polyimide module—feed pressure: 7.9 bar (100 psig); temperature: 30 °C; error range: ~8%.

Table 3

Feed, retentate and permeate CO<sub>2</sub> concentrations and CO<sub>2</sub>/CH<sub>4</sub> separation factors for different values of CO<sub>2</sub> feed concentrations in the Cardo-type hollow fiber polyimide module

|     | Feed CO <sub>2</sub> concentration 5 vol.% |                                     |                                                             | 10 vol.%                             |                                     |                                                             | 24.6 vol.% <sup>a</sup>              |                                     |                                                             |
|-----|--------------------------------------------|-------------------------------------|-------------------------------------------------------------|--------------------------------------|-------------------------------------|-------------------------------------------------------------|--------------------------------------|-------------------------------------|-------------------------------------------------------------|
|     | Retentate CO <sub>2</sub><br>(vol.%)       | Permeate CO <sub>2</sub><br>(vol.%) | Separation<br>factor<br>(CO <sub>2</sub> /CH <sub>4</sub> ) | Retentate CO <sub>2</sub><br>(vol.%) | Permeate CO <sub>2</sub><br>(vol.%) | Separation<br>factor<br>(CO <sub>2</sub> /CH <sub>4</sub> ) | Retentate CO <sub>2</sub><br>(vol.%) | Permeate CO <sub>2</sub><br>(vol.%) | Separation<br>factor<br>(CO <sub>2</sub> /CH <sub>4</sub> ) |
| Dry | 4.0                                        | 25.1                                | 7.2                                                         | 8.1                                  | 46.4                                | 9.1                                                         | 15.3                                 | 77.9                                | 15.0                                                        |
| Wet | 4.1                                        | 25.3                                | 7.2                                                         | 8.2                                  | 47.6                                | 9.1                                                         | 16.1                                 | 79.1                                | 15.0                                                        |

Cardo-type polyimide module—feed pressure: 7.9 bar (100 psig); temperature: 30 °C; saturator temperature: 25 °C; stage-cut: 5%.

<sup>a</sup> Stage-cut: 15%.

Table 4

Feed, retentate and permeate H<sub>2</sub>O concentrations and H<sub>2</sub>O/CH<sub>4</sub> separation factors for different values of CO<sub>2</sub> feed concentrations in the Cardo-type hollow fiber polyimide module

| Feed CO <sub>2</sub> (vol.%) | Feed H <sub>2</sub> O (vol.%) | Retentate H <sub>2</sub> O (vol.%) | Permeate H <sub>2</sub> O (vol.%) | Separation factor (H <sub>2</sub> O/CH <sub>4</sub> ) |
|------------------------------|-------------------------------|------------------------------------|-----------------------------------|-------------------------------------------------------|
| 0 (pure methane)             | 0.3                           | 0.2                                | 2.0                               | 8.9                                                   |
| 5                            | 0.3                           | 0.2                                | 2.2                               | 11.7                                                  |
| 10                           | 0.3                           | 0.2                                | 2.2                               | 13.9                                                  |
| 24.6 <sup>a</sup>            | 0.3                           | 0.13                               | 1.4                               | 25.7                                                  |

Cardo-type polyimide module—feed pressure: 7.9 bar (100 psig); temperature: 30 °C; saturator temperature: 25 °C; stage-cut: 5%.

<sup>a</sup> Stage-cut: 15%.

Because CO<sub>2</sub> is much more soluble in water than CH<sub>4</sub> it is expected that the rate of depression of CO<sub>2</sub> permeance due to the presence of water vapor be lower than that of CH<sub>4</sub>. That is, CO<sub>2</sub> partially dissolves in water and permeates through the membrane together with water molecules. However, the results from the current study indicated that this effect had been negligible.

Tables 3 and 4 tabulate CO<sub>2</sub> and H<sub>2</sub>O concentrations in the feed, retentate, and permeate streams in dry and wet cases for the Cardo-type polyimide hollow fiber module. The results indicated that the concentrations of streams were not affected by water vapor. For example, a feed stream with 5% carbon dioxide content was depleted to approximately 4% retentate in both dry and wet cases. On the other hand, the permeate was enriched in CO<sub>2</sub> to 25% in both cases.

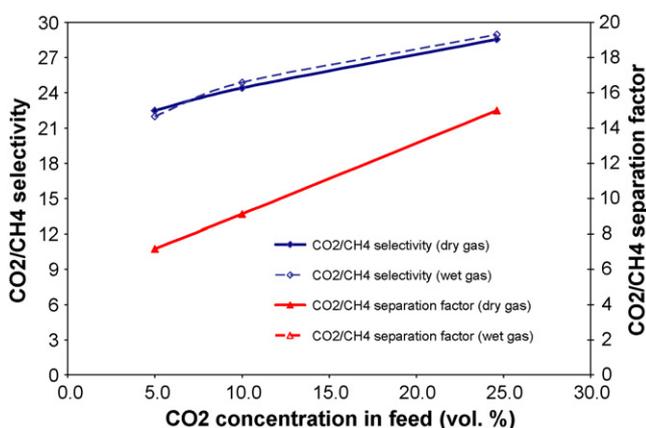


Fig. 4. CO<sub>2</sub>/CH<sub>4</sub> selectivity and separation factor vs. feed CO<sub>2</sub> concentration in the presence and absence of water vapor. Cardo-type polyimide module—feed pressure: 7.9 bar (100 psig); temperature: 30 °C; error range: ~11%.

Pure methane experiments at ambient temperature (~22.5 °C) and at 7.9 bar (100 psig) pressure were also carried out before and after the above series of experiments. It was concluded that the initial pure CH<sub>4</sub> permeance of 1.7 GPU was partially recovered to 1.6 GPU. The Cardo-type membranes used in the present study were relatively unaffected by relative humidity (~60%). This can be compared with the irreversible effects of 20% RH on cellulose acetate membranes as reported by Funk et al. [19].

Finally it would be interesting to compare the selectivity of Cardo-type polyimide membrane for CO<sub>2</sub>/CH<sub>4</sub> and other dry gas mixtures measured in this work and those reported in the literature. The obtained CO<sub>2</sub>/CH<sub>4</sub> selectivity for this polymer was 36, which is almost equal to that of CO<sub>2</sub>/N<sub>2</sub>, 38, that was reported by Kazama et al. [5] using the same type of membrane. The reported CO<sub>2</sub>/CH<sub>4</sub> selectivity for cellulose acetate and polysulfone membranes were reported by Story and Koros [6] to be 28 and 30, respectively.

#### 4.2. Polyphenylene oxide (PPO) hollow fibers

The effect of water vapor on CO<sub>2</sub>/CH<sub>4</sub> separation performance of hydrophobic PPO hollow fiber membranes was also investigated by carrying out pure CH<sub>4</sub> and CH<sub>4</sub>/CO<sub>2</sub> mixtures experiments in the absence and presence of water vapor. In this series of experiments, the stage-cut was set at 5%. The results are summarized in Figs. 5 and 6 and Tables 5 and 6. The reported data are the average of at least the last three readings after the steady state was reached, that took more than 2.5 h for PPO membranes.

From Fig. 5 it can be seen that the permeances of both CO<sub>2</sub> and CH<sub>4</sub> decreased in the presence of water vapor. However, the decrease was not as high as that in Cardo-type polyimide. As

Table 5  
Feed, retentate and permeate CO<sub>2</sub> concentrations and CO<sub>2</sub>/CH<sub>4</sub> separation factors for different values of CO<sub>2</sub> feed concentrations in PPO hollow fiber module

|     | Feed CO <sub>2</sub> concentration 5 vol.% |                                  |                                                       | 10 vol.%                          |                                  |                                                       | 24.6 vol.%              |                                  |                                                       |
|-----|--------------------------------------------|----------------------------------|-------------------------------------------------------|-----------------------------------|----------------------------------|-------------------------------------------------------|-------------------------|----------------------------------|-------------------------------------------------------|
|     | Retentate CO <sub>2</sub> (vol.%)          | Permeate CO <sub>2</sub> (vol.%) | Separation factor (CO <sub>2</sub> /CH <sub>4</sub> ) | Retentate CO <sub>2</sub> (vol.%) | Permeate CO <sub>2</sub> (vol.%) | Separation factor (CO <sub>2</sub> /CH <sub>4</sub> ) | CO <sub>2</sub> (vol.%) | Permeate CO <sub>2</sub> (vol.%) | Separation factor (CO <sub>2</sub> /CH <sub>4</sub> ) |
| Dry | 4.3                                        | 19.0                             | 4.8                                                   | 8.7                               | 35.3                             | 5.3                                                   | 22.3                    | 65.0                             | 6.1                                                   |
| Wet | 4.4                                        | 18.2                             | 4.6                                                   | 8.9                               | 34.1                             | 5.0                                                   | 23.3                    | 65.4                             | 6.0                                                   |

PPO module—feed pressure: 7.9 bar (100 psig); temperature: 30 °C; saturator temperature: 25 °C; stage-cut: 5%.

Table 6  
Feed, retentate and permeate H<sub>2</sub>O concentrations and H<sub>2</sub>O/CH<sub>4</sub> separation factors for different values of CO<sub>2</sub> feed concentrations in PPO hollow fiber module

| Feed CO <sub>2</sub> (vol.%) | Feed H <sub>2</sub> O (vol.%) | Retentate H <sub>2</sub> O (vol.%) | Permeate H <sub>2</sub> O (vol.%) | Separation factor (H <sub>2</sub> O/CH <sub>4</sub> ) |
|------------------------------|-------------------------------|------------------------------------|-----------------------------------|-------------------------------------------------------|
| 0 (pure methane)             | 0.3                           | 0.2                                | 2.0                               | 9.4                                                   |
| 5                            | 0.3                           | 0.2                                | 2.0                               | 9.3                                                   |
| 10                           | 0.3                           | 0.2                                | 2.1                               | 10.6                                                  |
| 24.6 <sup>a</sup>            | 0.3                           | 0.2                                | 1.8                               | 14.8                                                  |

PPO module—feed pressure: 7.9 bar (100 psig); temperature: 30 °C; saturator temperature: 25 °C; stage-cut: 5%.

<sup>a</sup> Stage-cut: 15%.

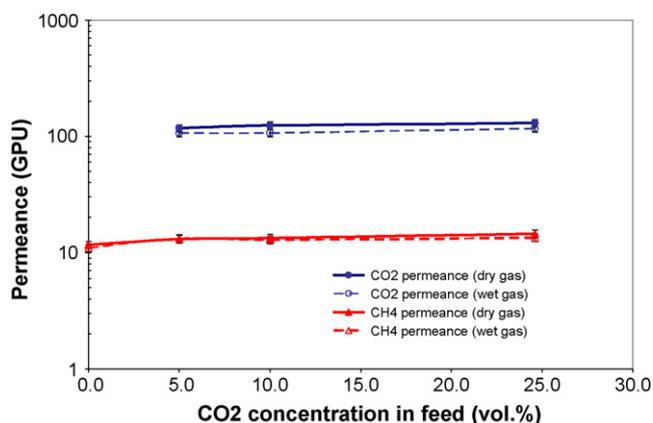


Fig. 5. CO<sub>2</sub> and CH<sub>4</sub> permeances vs. feed CO<sub>2</sub> concentration in the presence and absence of water vapor. PPO module—feed pressure: 7.9 bar (100 psig); temperature: 30 °C; error range: ~8%.

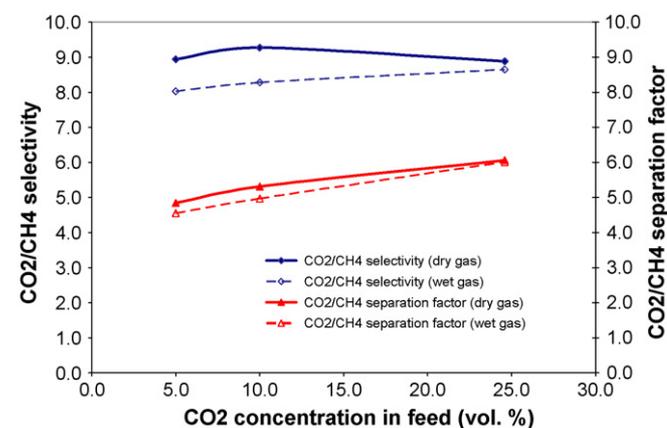


Fig. 6. CO<sub>2</sub>/CH<sub>4</sub> selectivity and separation factor vs. feed CO<sub>2</sub> concentration in the presence and absence of water vapor. PPO module—feed pressure: 7.9 bar (100 psig); temperature: 30 °C; error range: ~11%.

it was mentioned before, this phenomenon can be attributed to the hydrophobicity of PPO membranes. The CO<sub>2</sub> permeability decreased by as much as 11% in the presence of water vapor, while the CH<sub>4</sub> permeability showed only 1.5–7.5% decrease. According to the competitive sorption theory, the presence of water vapor affects the permeation of high affinity components to a greater extent compared with the permeation of low affinity ones. This theory is confirmed by the results of the present study where the permeation of CO<sub>2</sub> with higher affinity towards the membrane was affected more appreciably compared with that of the low affinity CH<sub>4</sub>. As a result, as it is seen in Fig. 6, the CO<sub>2</sub>/CH<sub>4</sub> selectivity and separation factor in the wet phase were lower than that of the dry phase.

Pure methane permeance was also decreased by 6% from 11.7 to 11.0 GPU for PPO hollow fiber membrane compared to 28% of the Cardio-type polyimide membrane.

Tables 5 and 6 tabulate CO<sub>2</sub> and H<sub>2</sub>O concentrations in the feed, retentate, and permeate streams in dry and wet cases for PPO membranes. The results indicated that the compositions of the streams remained almost the same and the PPO membrane performed almost independent of the presence and absence of water vapor.

## 5. Conclusions

The presence of water vapor in the feed stream significantly reduced the permeation rates of both CO<sub>2</sub> and CH<sub>4</sub> through hydrophilic Cardio-type polyimide hollow fiber membrane. The separation factor and selectivity, however, remained the same because the permeation rates of both gases were declined to the same extent.

A small decline in the permeation rate of CO<sub>2</sub> was observed through PPO hollow fiber membrane, but CH<sub>4</sub> permeation rate was not affected significantly. As a result, a decline in the separation factor and selectivity of this membrane was observed.

The reductions in the permeation rates were attributed to competitive sorption of the feed components and their preferential transport of the competing molecules across the membranes.

The permeances of pure methane through Cardo-type polyimide and PPO membranes declined 28% and 6%, respectively, when it was saturated with water vapor before entering the modules. It was observed that the initial permeance could not be fully recovered after the membrane was exposed to water vapor.

In an industrial application, drying a natural gas stream before feeding it into a membrane process enhances the separation efficiency of the system.

### Acknowledgments

The authors are grateful to Chaoyang Feng, Louis Trembley and Franco Ziroldo of the Department of Chemical Engineering of the University of Ottawa for their kind assistance in setting up the experimental apparatus. The courtesy of Parker Filtration and Separation B.V. of The Netherlands and the Research Institute of Innovative Technology for the Earth (RITE) of Japan for providing the membrane samples is highly appreciated. The first author is thankful to Sharif University of Technology for the scholarship and financial support that was provided to him during this research in Canada.

### References

- [1] A. Tabe-Mohammadi, A review of the applications of membrane separation technology in natural gas treatment, *Sep. Purif. Technol.* 34 (1999) 2095.
- [2] B.D. Bhide, A. Voskericyan, S.A. Stern, Hybrid processes for the removal of acid gases from natural gas, *J. Membr. Sci.* 140 (1998) 27.
- [3] W. Echt, Hybrid separation schemes for CO<sub>2</sub> removal: conditioning natural gas, *Chem. Eng.* (2002) 46.
- [4] M. Pourafshari Chenar, M. Soltanieh, T. Matsuura, A. Tabe-Mohammadi, C. Feng, Gas permeation properties of commercial polyphenylene oxide and Cardo-type polyimide hollow fiber membranes, *Sep. Purif. Technol.*, in press.
- [5] S. Kazama, T. Teramoto, K. Haraya, Carbon dioxide and nitrogen transport properties of bis(phenyl)fluorine-based Cardo polymer membranes, *J. Membr. Sci.* 207 (2002) 91.
- [6] B.J. Story, W.J. Koros, Sorption and transport of CO<sub>2</sub> and CH<sub>4</sub> in chemically modified poly(phenylene oxide), *J. Membr. Sci.* 67 (1992) 191.
- [7] Y. Tokuda, E. Fujisawa, N. Okabayashi, N. Matsumiya, K. Takagi, H. Mano, K. Haraya, M. Sato, Development of hollow fiber membranes for CO<sub>2</sub> separation, *Energy Convers. Manage.* 38 (1997) S111.
- [8] S. Karashima, Y. Tokuda, A. Tachiki, K. Takagi, K. Haraya, C. Kamizawa, Development of Cardo-type polyimide hollow fiber membranes for CO<sub>2</sub> separation, in: P. Riemer, B. Eliasson, A. Wokaun (Eds.), *Greenhouse Gas Control Technologies*, Elsevier Sci. Ltd., 1999, p. 1035.
- [9] S. Mortazavi, Development of polyphenylene oxide and modified polyphenylene oxide membranes for dehydration of methane, PhD Thesis, University of Ottawa, 2004.
- [10] M. Aguilar-Vega, D.R. Paul, Gas transport properties of polyphenylene ethers, *J. Polym. Sci. B: Polym. Phys.* 31 (1993) 1577.
- [11] R.W. Baker, *Membrane Technology and Applications*, John Wiley & Sons Ltd., 2004.
- [12] G. Chowdhury, B. Kruczek, T. Matsuura, *Polyphenylene Oxide and Modified Polyphenylene Oxide Membranes: Gas, Vapour and Liquid Separation*, Kluwer Academic Publishers, 2001.
- [13] N.A. Plate, Y. Yampolskii, High free volume polymers, in: D.R. Paul, Y. Yampolskii (Eds.), *Polymer Gas Separation Membranes*, CRC Press, London, 1994.
- [14] W.J. Koros, R.T. Chern, V. Stannett, H.B. Hopfenberg, A model for permeation of mixed gases and vapors in glassy polymers, *J. Polym. Sci.* 19 (1981) 1513.
- [15] D.G. Pye, H.H. Hoehn, M. Panar, Measurement of gas permeability of polymers. II. Apparatus for determination of permeabilities of mixed gases and vapors, *J. Appl. Polym. Sci.* 20 (1976) 287.
- [16] S.J. Metz, J. Potreck, M.H.V. Mulder, M. Wessling, Water vapor and gas transport through poly(butylenes tetraphthalate) poly(ethylene oxide) block copolymer, *Desalination* 148 (2002) 303.
- [17] B. Kruczek, T. Matsuura, Limitations of a constant pressure-type testing system in determination of gas transport properties of hydrophilic films, *J. Membr. Sci.* 177 (2000) 129.
- [18] R.T. Chern, W.J. Koros, E.S. Sanders, R. Yui, Second component effects in sorption and permeation of gases in glassy polymers, *J. Membr. Sci.* 15 (1983) 157.
- [19] E.W. Funk, S.S. Kulkarni, A.X. Swamikannu, Effect of impurities on cellulose acetate membrane performance, *AIChE Symp. Series No. 250*, 1986.
- [20] W.A. Dietz, Response factors for gas chromatographic analyses, *J. Gas Chromatogr.* (1967) 68.